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RESEARCH ON THE ELECTRONIC CONFIGURATION IN THE FERROMAGNETIC MATERIALS

By

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Background

Many years ago the fact was established[1/] that the Hall effect in ferromagnetic materials at low magnetic fields was proportional to the magnetization, M, within the limits of the available accuracy. This appeared to be contrary to theory, which predicted that the effect should be proportional to B or H and should be much smaller than was observed. The author started this research project because of his belief that the theoretically predicted effect must exist and could be separated from the larger effect, usually observed if sufficiently precise measurements could be made in magnetic fields well above those required to saturate the material. He further believed that the smaller effect would give information concerning the electronic configurations in these materials that could not be obtained any other way.

Resume of Results

Experiments have shown that both of these beliefs were well founded. Accurate measurements on Ni separating the small theoretically predicted effect from the larger usually observed effect were made by Schindler and the author in 1950. The newly observed effect was named the "ordinary" effect because it is the one ordinarily observed in other materials, while the large unexplained effect was named the "extraordinary" effect. The ordinary effect in Ni agreed with predictions to within a factor of two, in contrast

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1/ Emerson M. Pugh, "Hall Effect and the Magnetic Properties of some Ferromagnetic Materials," Phys. Rev. 36, 1503-1511 (Nov. 1930). E. M. Pugh and T. W. Lippert, "Hall emf and Intensity of Magnetization," 42, 709-713 (Dec. 1932).

to the results previously obtained with the extraordinary effect which were from 10 to 100 times larger.

A careful search of old literature revealed that some early Hall data by A. W. Smith[2/] showed essentially the same results as were obtained here. His data could be analyzed into its ordinary and extraordinary parts. This was reported in Tech. Rep. No. A-1.

A more thorough analysis of the old Smith data yielded evidence that the ordinary coefficient in Ni changes very little temperature from very low temperatures up through the Curie temperature, provided the observed anomaly very close to the Curie temperature was due to the fact that $\alpha\, \partial M/\partial B$ is not small even at high magnetic fields near the Curie temperature. This analysis was reported in Tech. Rep. No. A-2.

The relationships between the Hall effect and the ponderomotive force on simple metals carrying currents in magnetic fields was analyzed and reported in Tech. Rep. No. A-3.

Much work had to be done to install an A. D. Little, 135 KW magnet together with field stabilizing devices and with very sensitive and very stable voltage measuring circuits, before accurate measurements of the ordinary and extraordinary Hall coefficients could be made on the binary alloys of Cu, Ni, Co and Fe. While this work was progressing, measurements were made on a nickel ferrite. Sufficient measurements had been obtained on the ferromagnetic metals to convince us of the reality of the two Hall effects

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2/ A. W. Smith, Phys. Rev. 30, 1 (1910).

in these materials. The nickel ferrite results showed that ferromagnetic semiconductors exhibit the same two Hall effects. This work was reported in Tech. Rep. No. A-4.

Room temperature measurements on Cu-Ni alloys were completed and analyzed by Schindler. They showed that the ordinary coefficients agreed with current theories to within a factor of two. In fact, if proper corrections could be made to the data on the alloys, from 10 percent Ni to 90 percent Ni in Cu, these ordinary coefficients agreed with theory to within 20 percent. The need for measurements on these materials over a wide range of temperatures was obvious. The extraordinary coefficients (α's) were found to increase from $\backsim$ 10 for pure Ni to $\backsim$ 60 for 70 Ni-30 Cu at room temperatures. Over a small range of temperatures these α's all show the same tendency to increase rapidly with temperature. This work was reported in Tech. Rep. No. 1 (Albert I. Schindler's thesis) and in Tech. Rep. No. A-5.

A summary of data and conclusions that had been obtained by the fall of 1952, was reported at the ONR Conference on Magnetism, University of Maryland and this summary was reported in Tech. Rep. No. A-6.

Room temperature measurements on Co-Ni alloys were completed and analyzed by Simon Foner. Again the ordinary coefficients agreed to within a factor of two with predictions from current theories. However, the fact that many of these coefficients were twice the expected negative value could not be explained even by invoking two band conduction. A possible explanation of this anomaly was presented to the Gordon Conference on Band Structures in 1953.

The paper being prepared for publication on this subject is included as part of this report.

The extraordinary coefficients in the Co-Ni alloys have small absolute values and change sign between 20 percent and 40 percent Co in Ni. Their absolute values show the usual increase with temperature. These results were presented in Tech. Rep. No. 2 (Simon Foner's thesis) and in Tech. Rep. No. A-7.

Measurements on the Cu-Ni alloys at temperatures of 4 ^{o}K, 20 ^{o}K, 77 ^{o}K and room temperature have been completed and analyzed by Philip Cohen. The thesis and publication as yet have not been completed. The significant results, however, are included in the attached manuscript that has been prepared for publication. This manuscript contains an analysis of the experimental results obtained to date, together with an explanation of these results based upon a simplified band picture.

List of Technical Reports

1. "The Hall Effect of Copper Nickel Alloys," by Albert I. Schindler (Thesis June 1951).

2. "Hall Effects of the Cobalt Nickel Alloys and of Armco Iron," by Simon Foner (Thesis June 1952).

A-1. Emerson M. Pugh, N. Rostoker and A. Schindler, Phys. Rev. 80, 4, 688-692 (Nov. 15, 1950).

A-2. N. Rostoker and Emerson M. Pugh, Phys. Rev. 82, 1, 125-126 (Apr. 1, 1951).

A-3. Norman Rostoker, Am. Jour. of Phys. 20, 2, 100-107 (Feb. 1952).

A-4. Simon Foner, Phys. Rev. 88, 4, 955-956 (Nov. 15, 1952).

A-5. A. I. Schindler and Emerson M. Pugh, Phys. Rev. 89, 1, 295-298 (Jan. 1, 1953).

A-6. Emerson M. Pugh and Norman Rostoker, Rev. Mod. Phys. 25, 1, 151-157 (Jan. 1953).

A-7. Simon Foner and Emerson M. Pugh, Phys. Rev. 91, 1, 20-27 (July 1, 1953).

Recommendations

The work that should now be done in this field seems limitless. If the analysis based upon a rather simple band picture proves to be valid, these methods can provide a large quantity of information concerning the electronic configurations in this transition group of elements and their alloys. Measurements are needed to test the validity of the band picture and to provide information on the electronic configurations. Some of the most urgent experiments are listed below.

1. Several of the alloys should be taken through their Curie temperatures, especially those whose ordinary coefficients are large negative values ($n^* \cong 0.3$).
2. Measurements should be extended to lower electronic concentrations; i.e. to the Fe-Co, Fe-Mn and Fe-Cr alloys.
3. Measurements should be made to compare results on different alloys having the same electronic concentration; e.g. compare 50 Co-50 Ni with 25 Fe-50 Ni, etc.

A Band Model for Explaining Data from Hall Effect, Magnetization, and Resistivity Measurements on Magnetic Elements and Their Binary Alloys.

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Abstract

The ordinary Hall coefficients for Cu, Ni, Co and the binary alloys of these elements agree to within a factor of two with predictions based upon the usual band model in which the number of conduction electrons per atom is postulated to be the number, $n_s = 0.6$, of 4s electrons required to explain the saturation magnetization in these materials. The factor of two, however, created a dilemma, since both the magnetization data and the Hall data were accurately determined. The Hall results appeared to require that $n_s < 0.3$ whereas the magnetization data requires that $n_s > 0.54$. It will be shown that this dilemma disappears when the 4s band is considered divided into two parts in which the electrons with spins parallel to the spontaneous magnetization have much greater mobility than those with spins antiparallel. According to Mott, the antiparallel electrons have low mobility, because they can be scattered into the partially empty 3d band, whereas the parallel electrons cannot.

It will be shown that the ordinary Hall data, the saturation magnetization data, and the resistivity data for these transition elements and their alloys, can be made understandable by employing a four band model, consisting of two 4s bands and two bands from the 3d shell.

Introduction

Hall effect measurements[1,2], on Ni, Co, Fe and on the binary alloys of Cu-Ni and Ni-Co, have yielded the two different coefficients R_o and R_1 in the expression[3] for the Hall emf,

$$E_H = (R_o H + R_1 M)\, I/t \quad ,$$

where H is the magnetizing field, M is the intensity of magnetization in the sample, I is the current in the sample and t is the thickness of the sample.

The ordinary coefficient R_o is positive in Fe[2], indicating hole conduction, but is negative in all of the rest of these materials. Except in Fe, these ordinary coefficients are in agreement, within a factor of two[4], with the predictions of a simple one-band model in which the 4s electrons (0.6 per atom) are the carriers. For this one-band model the ordinary coefficients are given by

$$R_o = 1 \,/\, N n_s e c \qquad (1)$$

where N is the number of atoms per cc, e is the absolute value of the electronic charge and c is the velocity of light. The number of conduction electrons per atom, $n_s \cong 0.6$, is obtained from the saturation magnetization of these materials at low temperatures. Within this factor of two, there are systematic variations in R_o with electronic concentration, which show that the Hall effect must be complex in these materials.

1/ A. I. Schindler and E. M. Pugh, Phys. Rev. 89, No. 1, 295-298, Jan. 1, 1953.

2/ Simon Foner and Emerson M. Pugh, Phys. Rev. 91, No. 1, 20-27, July 1, 1953.

3/ Emerson M. Pugh, Phys. Rev. 36, No. 9, 1503-1511, Nov. 1, 1930.

4/ Emerson M. Pugh and Norman Rostoker, Rev. of Mod. Phys. 25, No. 1, 151-157, Jan. 1953, and also refs. 1 and 2.

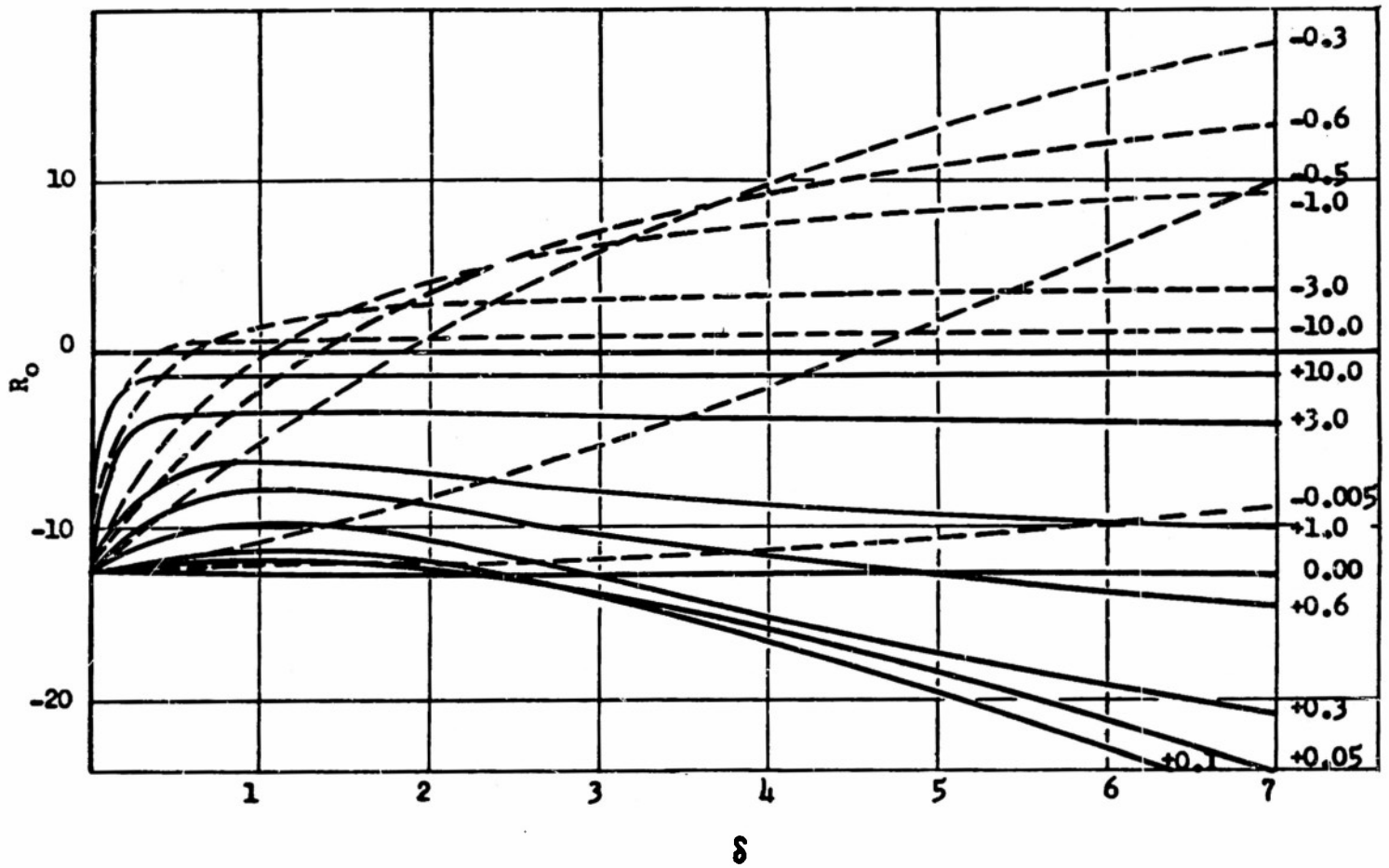
10
0
-10
-20
R_o
1
2
3
4
5
6
7
δ
-0.3
-0.6
-0.5
-1.0
-3.0
-10.0
+10.0
+3.0
-0.005
+1.0
0.00
+0.6
+0.3
+0.1
+0.05

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Fig. 1 Calculations of the ordinary Hall constant, R_o, for two band models in which the first band always contains 0.56 electron/atom, while the second band contains different numbers of either holes or electrons. The R_o's are plotted against δ, the relative mobility in the second band compared to the first. The different curves are designated by the ratio obtained by dividing the number of carriers/atom in the second band by 0.56, the ratio being positive (solid lines) for electrons and negative (dotted lines) for holes. The $|R_o|$'s are not as great as that for the first band alone until δ considerably exceeds unity. This is a general conclusion for two band models.

The fact that the ordinary coefficient in Fe is positive[5] suggests that the Hall effect in the other materials may be affected by conduction in the 3d band as well as in the 4s band. An attempt to correlate the data, using the Jones-Zener equation[6] for the Hall coefficient, with two-band conduction showed that the data could not be explained with $n_s = 0.6$. In fact, if one assumes that the mobility of the 4s electrons is greater[7] than the mobility of either the electrons or holes in the 3d band, the data can be explained only by taking $n_s < 0.3$.

To show this, values of the Hall coefficient for a two-band model are calculated from the Jones-Zener equation and are plotted in Fig. 1 as functions of $\delta (= \mu_d/\mu_s)$, the ratio of the mobility in the 3d band to the mobility in the 4s band. In making these calculations the number of 4s electrons per atom has been kept constant, while the number of 3d holes or of 3d electrons per atom have been varied over the complete range of possible values. In this figure, dashed lines are used for the hole conduction and solid lines for the electronic conduction in the 3d band. Each curve is labeled with a ratio representing the number of 3d carriers/atom, used in calculating the curve, divided by 0.54, the assumed number of 4s electrons/atom. The sign of this ratio is taken as positive

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5/ The Hall coefficient is also positive in Mn, Cr, V and Ti.

6/ Jones and Zener, Proc. Roy. Soc. A, 145 (1934) 269, eq. 4.

7/ While this assumption is most reasonable, the same conclusions are reached with a much less restrictive assumption; namely, that the mobility in the 3d band is not more than 4 or 5 times as great as the mobility in the 4s band.

when the 3d carriers are electrons and negative when they are holes. The number $n_s = 0.54$ is used because new measurements on the g-factor[8] show that n_s may be as small as 0.54 electrons/atom. If as assumed, the 4s band mobility is greater than the 3d band mobility ($\delta = \mu_d/\mu_s < 1$), only those parts of the curves extending from $\delta = 0$ to $\delta = 1$ are of interest. It is obvious that this equation cannot account for values of R_o below -13×10^{-13} ohm-cm/oersted, with $n_s \geq 0.54$, although values below -20×10^{-13} ohm-cm/oersted are observed in both Ni-Cu and Ni-Co alloys. A value of $n_s < 0.3$ is required to account for the R_o values. Thus the two-band model can account for the Hall data only with $n_s < 0.3$, while it can account for the saturation magnetization of these alloys only with $n_s > 0.54$.

At a conference[9] last summer the author proposed that this dilemma could be solved by separating the 4s band into two equal parts according to the spins of the electrons. Those 4s electrons with spins parallel to the spontaneous magnetization, according to Mott[10] have mobilities much greater than the electrons with spins antiparallel, since the latter can be scattered into the partly empty 3d band. Since the parallel 3d band is full at low temperatures the parallel electrons cannot be scattered into it. A. Bloembergen[9] pointed out that if the above were the correct explanation

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8/ "Introduction to Solid State Physics," by C. Kittel, J. Wiley and Sons (1953) p. 171 and also "Ferromagnetism" by R. M. Bozorth, D. Van Nostrand Co. (1951) p. 809.

9/ Gordon Conference, New Hampton, N.H., July 1953. The author is indebted to several of the scientists who participated in this conference for many stimulating discussions. The verbal suggestion by A. Bloembergen concerning temperature dependence proved to be especially fruitful.

10/ N. F. Mott, Proc. Roy. Soc., London A, 153, 699-717 (1936).

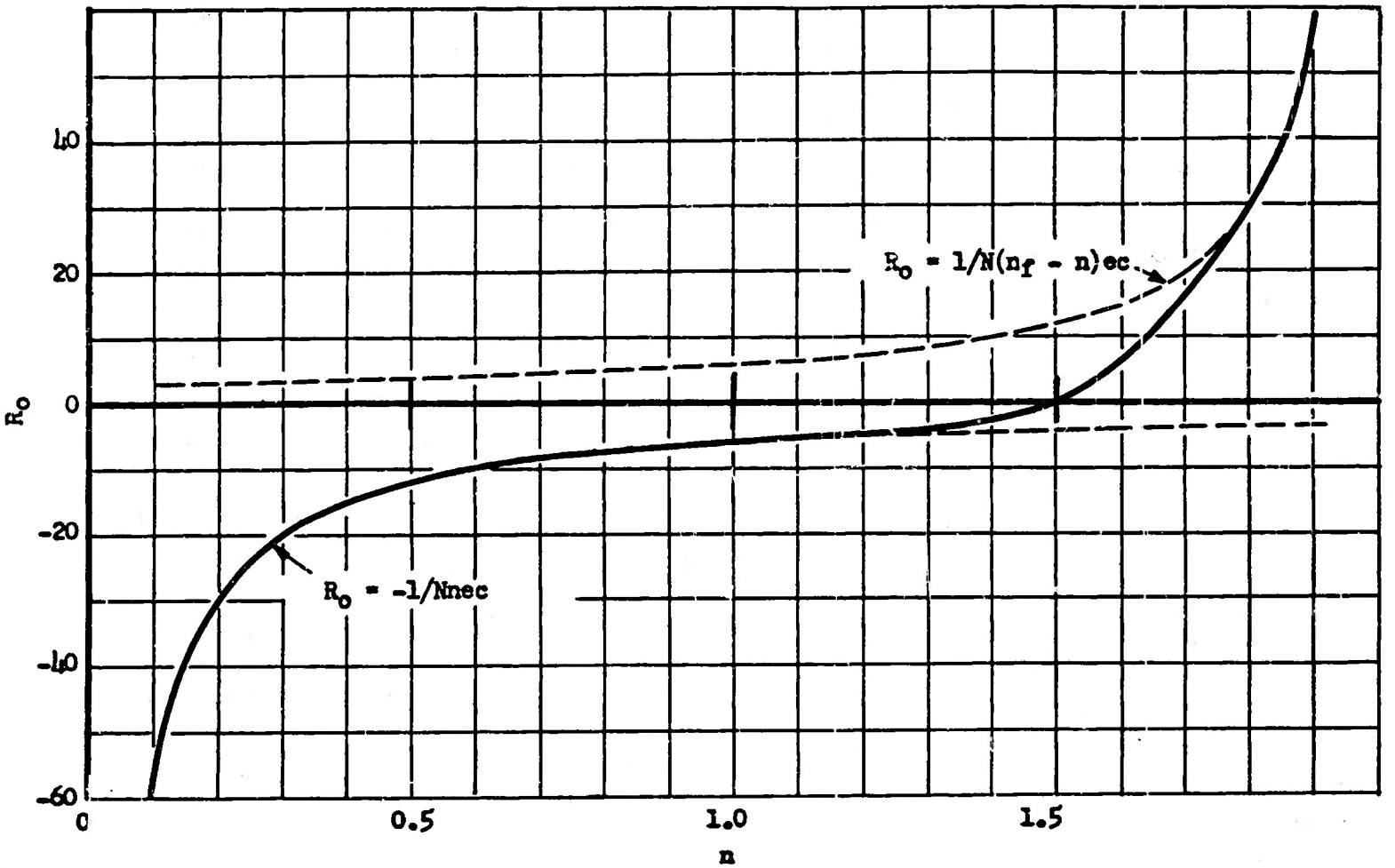

Fig. 2 Calculations of the ordinary Hall constant, R_o, for single band conduction as a function of the number of electrons in the band. Near the bottom of the band $R_o = -1/Nnec$, while near the top of the band $R_o = 1/N\ (n_f - n)ec$. In between the curve changes sign by going through zero.

of the data, then R_o in these materials should vary with temperature from a value corresponding to $n_s \cong 0.27$ at low temperatures to a value corresponding to $n_s \cong 0.54$ above the Curie temperature. Philip Cohen in this laboratory has completed measurements[11/] from 4 °K to room temperature on the Cu-Ni alloys, which verify this predicted temperature dependence for the magnetic alloys and the expected lack of temperature dependence for the non-magnetic alloys. Furthermore the absolute values of R_o are within 15 percent of the values predicted by such a model for all but the pure copper. In copper the measured Hall coefficient is only 2/3 of the predicted value. There are at least two reasons for expecting the measured Hall coefficient in copper to be smaller than predicted by this simple model; first, the value would be reduced markedly if there is a small amount of conduction in the 4p band, second, the value might be reduced by the inaccuracies in the approximation of Eq. (1). This equation is a good approximation only when the band is not too full. A similar approximation holds when the band is nearly full. As a band is filled up the value of R_o for that band passes through zero and becomes positive. The behavior of R_o versus n for a single conduction band in a simple cubic crystal as calculated by Rostoker on the basis of the tight-binding approximation[12/], is shown in Fig. 2. When n is small as in a nearly empty band

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11/ Philip Cohen, Thesis, "Hall Effects of Cu, Ni and the Cu-Ni Alloys at Low Temperatures," Carnegie Institute of Technology, June 1954.

12/ Unpublished private communication from N. Rostoker.

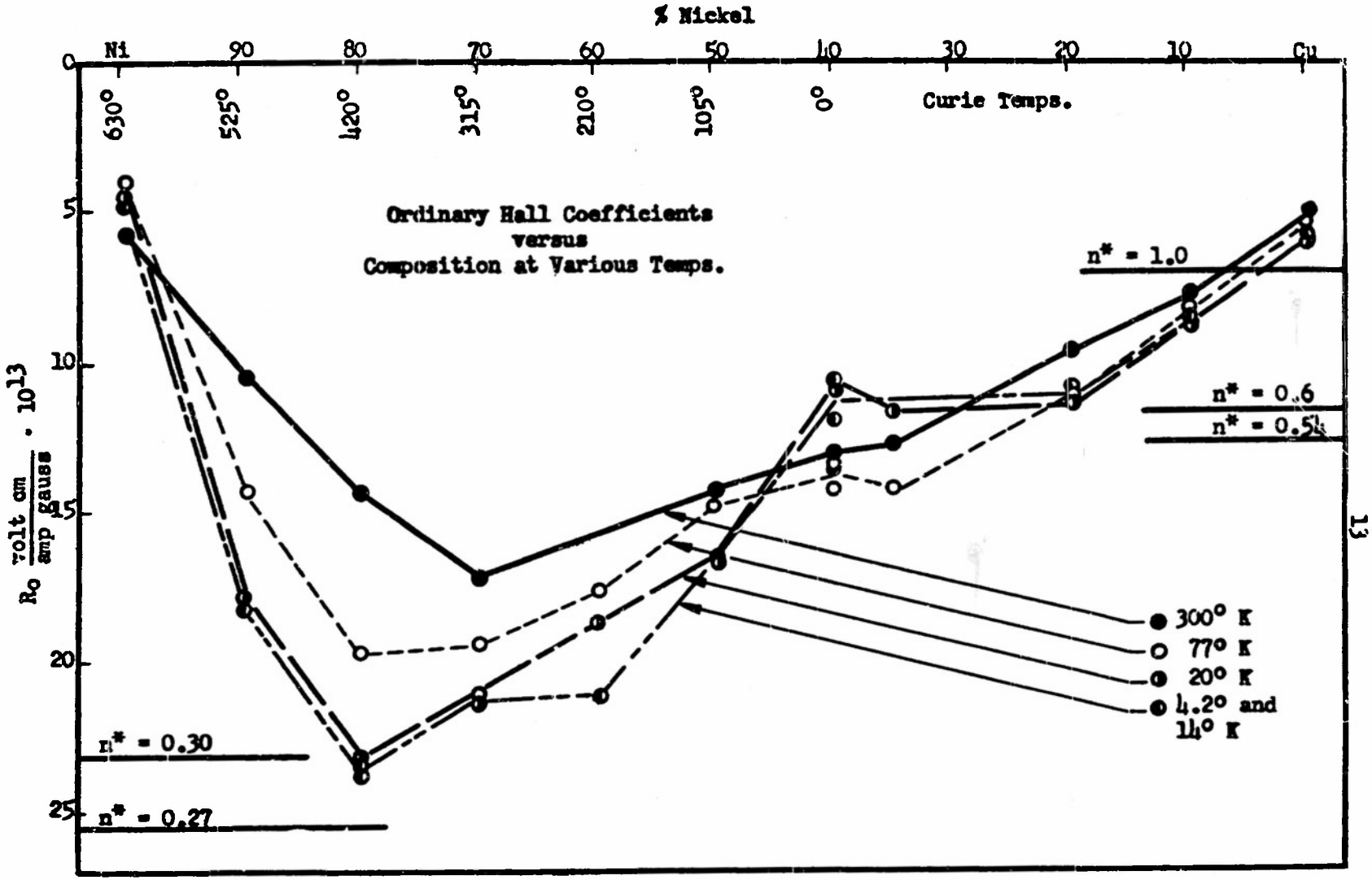

Fig. 3 Ordinary Hall coefficients for Ni-Cu alloys measured at various temperatures by Schindler and Cohen. Lines are drawn to show the values of R_o corresponding to certain n^*'s, where $n^* = -1/R_o Nec$.

Eq. (1) is a very excellent approximation. When n is nearly equal to n_f, the number of electrons required to fill the band, the equation

$$R_o = 1 / Nec(n_f - n) \qquad (2)$$

is an excellent approximation. For crystals other than the simple cubic, very good approximations for R_o are obtained from Eq. (1) for a single conduction band that is not too full and from Eq. (2) when the band is nearly full. Between the two extremes the calculations are difficult and the results are more uncertain. For real crystals R_o goes through zero at some point above $n = n_f/2$ as suggested by the dotted line in Fig. 2. From Fig. 2 it is not too surprising that most of the metals with half filled s bands, like Cu, Ag and Au, show absolute values of R_o that are less[13] than those given by Eq. (1). Fortunately, in the region where the uncertainty in Eq. (1) is greatest the values of R_o are small. This fact is of great importance when multiple band models are being analyzed.

The Hall effect in Cu, Ni, and some Cu-Ni alloys has been measured by Schindler[14] at room temperatures and by P. Cohen[11] at low temperatures. Their combined results for R_o versus composition

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13/ Lithium appears to be an exception, for the reported absolute values of R_o are larger than expected from Eq. (1). It should be worth investigating whether or not some common impurity in Li could be responsible for this result.

14/ A. I. Schindler and E. M. Pugh, Phys. Rev. 89, 295 (1953). Some very accurate thickness measurements were made on the samples after this paper was published. The corrected values for all measurements are given in Fig. 3.

are plotted in Fig. 3. The values at liquid helium temperatures are now understandable. As the percent Ni in Cu increases from zero to 40 percent the number of 4s electrons per atom, n_s, decreases from ~1.0 to ~ 0.6. At the same time R_o increases from $5.95 \pm 0.08 \times 10^{-13} \frac{\text{volt cm}}{\text{amp oersted}}$ for pure Cu to $13.1 \pm 0.1 \times 10^{-13} \frac{\text{volt cm}}{\text{amp oersted}}$ for the 40 percent Ni alloy. The latter figure corresponds to an $n^* = 1/R_oNec$ of 0.56 ± 0.05. As the Ni content is increased beyond 40 percent the antiparallel half of the 3d band begins to empty. This reduces the mobility of the antiparallel 4s electrons, because they can now be scattered into the 3d band. The mobility of the parallel 4s electrons remains high since they cannot be so scattered. Thus with increasing Ni content beyond 40 percent, R_o gradually becomes more negative and reaches the value $23.7 \times 10^{-13} \frac{\text{volt cm}}{\text{amp oersted}}$ which corresponds to an n^* of 0.29, when the Ni content reaches 80 percent. Apparently in this alloy the ordinary effect is due almost entirely to those 4s electrons that have parallel spins. The mobility of the other carriers can be ignored. As the Ni content of these alloys is increased from 40 percent to 80 percent, the change of n^* from 0.56 to 0.29 takes place gradually, since at first the number of scattering centers in the antiparallel 3d band is small, so that the influence of the antiparallel 4s electrons disappears slowly. As the Ni content is increased beyond 80 percent, hole conduction in the antiparallel 3d band becomes increasingly important and reduces the absolute value of R_o. This should be expected from the calculations plotted in Fig. 1. A more complete discussion of behavior of pure Ni will be given in a later paragraph.

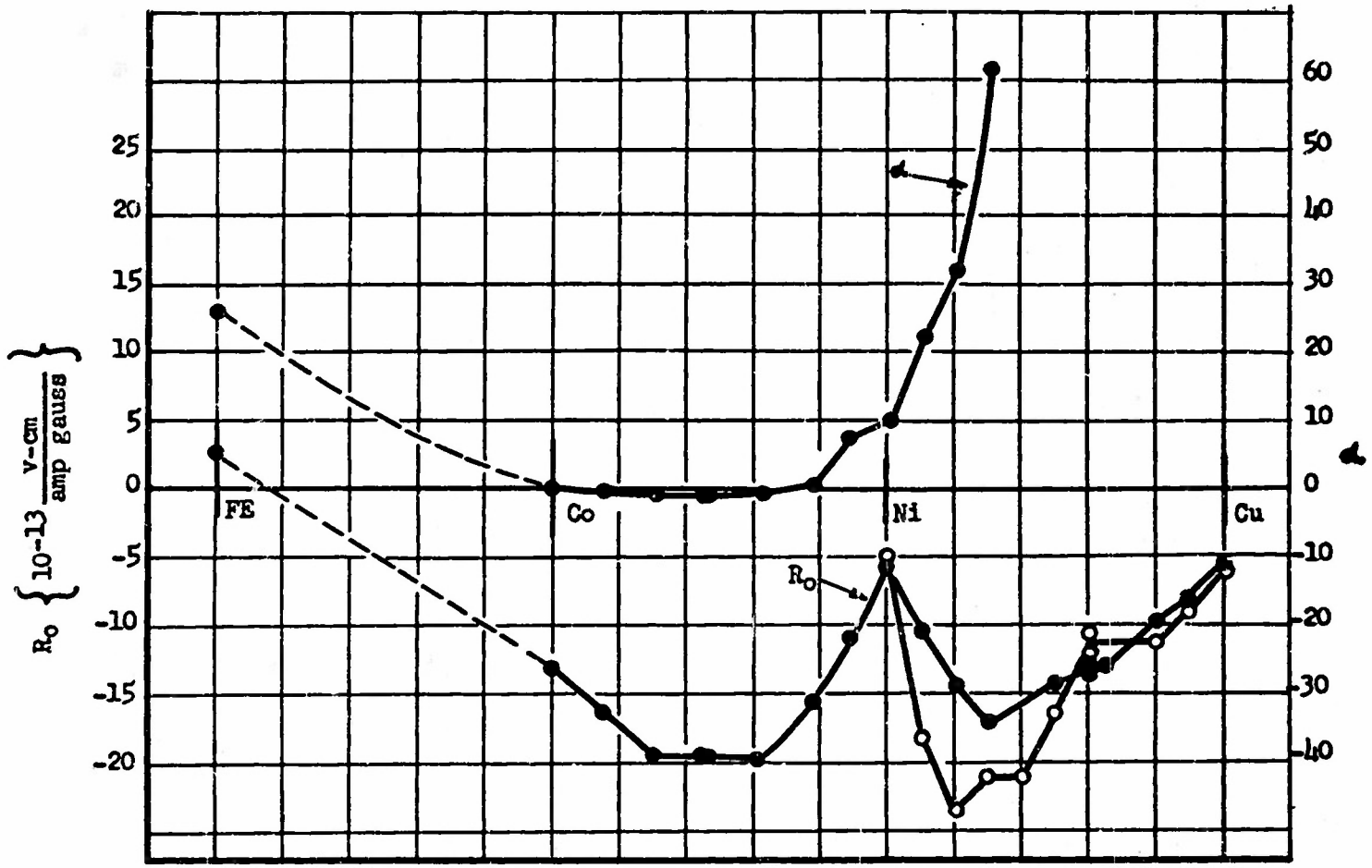

Fig. 4 Ordinary Hall coefficients for Fe, Co-Ni alloys and Cu-Ni alloys plotted against electron concentrations. Open circles were obtained at 4°K and solid circles were obtained at room temperature. The field parameters, α's, were obtained at room temperature.

It is seen that the large negative values of R_o for the Cu-Ni alloys, whose compositions lie between 50 and 90 percent Ni, are due to 4s electrons with parallel spins having greater mobilities than those with antiparallel spins. This is true only at temperatures far below the Curie points. As temperatures approach the Curie temperatures, the two mobilities should approach each other and produce smaller ordinary Hall coefficients corresponding to conduction by all the 4s band electrons with n^* between 0.54 and 0.60. Thus in these alloys $|R_o|$ decreases with temperature up to the Curie point.

The electron concentration per atom can be reduced below that in pure Ni by adding Co ($Z = 27$) to the Ni ($Z = 28$). Foner and Pugh[2] have measured Ni-Co alloys at room temperature. Since these alloys have fairly high Curie temperatures, room temperatures can be considered as relatively low. Foner's data is plotted in Fig. 4. The fact that R_o again approaches -20×10^{-13} ohm-cm/oersted corresponding to $n^* \cong 0.35$, suggests that the 3d contribution to the conduction which is so prominent in Ni, passes through zero[15] somewhere between 25 and 50 percent Co in Ni and becomes negative with increasing Co content thereafter. The Jones-Zener equation

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15/ It is significant that the extraordinary coefficient R_1 also changes sign in this same neighborhood. Luttinger and Karplus, (J. M. Luttinger, Hall Effect in Ferromagnetics, Am. Phys. Soc. Bulletin; Jan. 28, 1954, p. 45) have shown that scattering within the 3d band is primarily responsible for the values of R_1. Apparently R_1 becomes zero at approximately the electronic concentration, where contribution of the 3d band to R_o becomes zero.

This point where the ordinary Hall coefficient for the top 3d sub-band passes through zero should be near the maximum of the density of states curve.

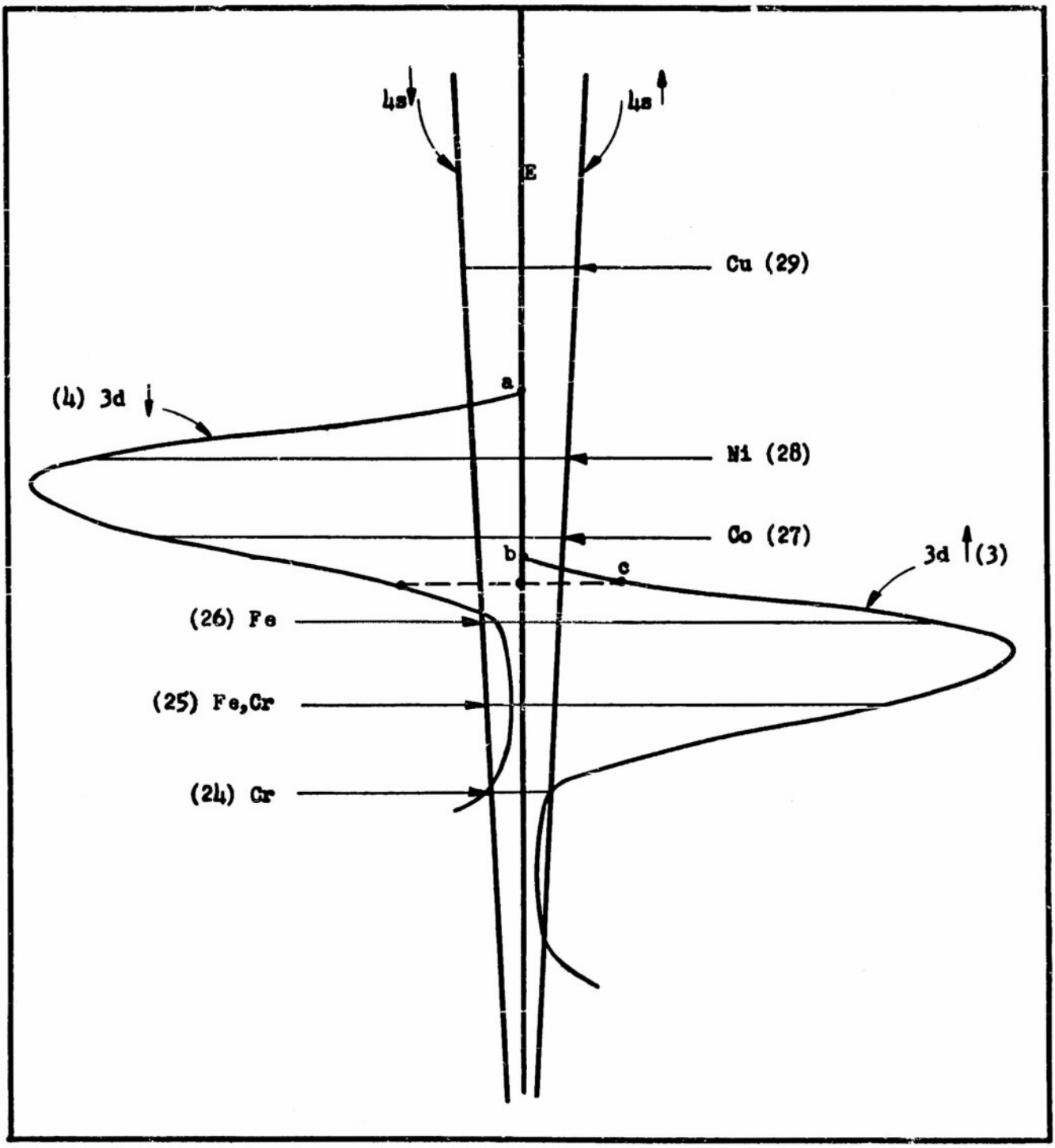

Fig. 5 Assumed density of states versus energy curves for the two 4s and the two 3d bands used in analyzing the data. The bands with spinsparallel to the field are plotted to the right while those with antiparallel spins are plotted to the left of the energy axis.

plotted in Fig. 1 shows that if there is either electronic or hole conduction in the 3d band, it will tend to reduce the absolute magnitude of R_o. As can be seen from the solid lines in Fig. 1, 3d electrons having a given mobility are less effective in reducing $|R_o|$ than are 3d holes having the same mobility. This may account for the fact, shown in Fig. 4, that the absolute value of R_o reduces very slowly with composition as pure Co is approached.

In the foregoing analysis it has been assumed tacitly that in ferromagnetic metals the electrical conduction can be described by four groups of carriers, each having its own characteristic mobility and its own characteristic Hall constants. The need for four instead of two groups of carriers lies in the fact that antiparallel electrons may have mobilities different from those of the parallel electrons in both the 3d and the 4s bands. The assumption that the conduction carriers can be separated into groups is a commonly used device for analysing data that is too complex for a more sophisticated treatment. Some justification for assigning separate Hall constants and separate mobilities to each of these groups is found in the fact that this treatment for two bands leads to the same equation as that obtained by Jones and Zener.

For the purpose of this analysis the density of states versus energy curves for the 3d and 4s bands of these transition metals may be divided into four curves somewhat as shown in Fig. 5. The density of those states with spins parallel to the spontaneous magnetization are plotted to the right of the vertical axis, while those with spins antiparallel are plotted to the left. Because there is no net spin in the 4s band the two 4s band curves are

symmetrical about the energy axis. Presumably the 3d curves are also symmetrical in shape though the parallel curve is displaced to lower energies because of exchange interactions. The Hall data can be explained more simply if the two 3d bands which contribute to the conduction process are sub-bands, each containing between 2 and 3 electronic states/atom.

It can be seen that such a model readily explains the existing ordinary Hall effect data. It also provides the usual collective electron interpretation of the fact that the saturation magnetization at low temperatures in Cu-Ni and Ni-Co alloys is a linear function of the electron concentration. In addition the model provides a simple explanation of that part of the Slater-Pauling curve which shows decreasing saturation magnetization toward the lower values of electron concentration.

As the electron concentration is reduced from 29 per atom at Cu to 28.6, the number of 4s electrons/atom is reduced from 1.0 to 0.6 at which point the Fermi level reaches point a in Fig. 5. As the Fermi level descends from a to b the antiparallel 3d shell begins to empty leaving a net parallel spin. Thus the saturation magnetization increases linearly. From b to c the net spin increases more and more slowly because electrons are being removed with increasing rapidity from the parallel 3d band with decreasing rapidity from the antiparallel. The maximum net spin occurs at c where the rates of removal of electrons from the two bands become equal. When the top sub-band of the antiparallel d shell becomes empty near Fe, the top sub-band of the parallel d shell empties more rapidly. The reduction in saturation magnetization

should be linear except for the few antiparallel electrons that may still be removed from the antiparallel band.

Four Band Model

Because of the different mobilities in the two halves of the 4s band and because of the different numbers of carriers and their different mobilities in the top two 3d sub-bands, a four band model is required. It is assumed that ordinary coefficients R_{o1}, R_{o2}, R_{o3} and R_{o4} can be defined for the four bands, each of which behave like the R_o in Fig. 2. The subscripts 1, 2, 3 and 4 refer to the parallel half of the 4s band, the antiparallel half of the 4s band, the parallel half of the top 3d sub-band and the antiparallel half of the top 3d sub-band, respectively. The number of electrons per atom in these bands, when filled, are $n_{f1} = n_{f2} = 1$ and $n_{f3} = n_{f4}$. For completeness it will also be assumed that associated with each of these bands, there are extraordinary Hall coefficients R_{11}, R_{12}, R_{13} and R_{14}. Whenever the ordinary Hall effect alone is being considered, this last assumption has no effect upon the results.

The measured Hall emf divided by the distance between the Hall probes can be written

$$E_y = R_o H \sigma E_x + R_1 M \sigma E_x \qquad (3)$$

where E_x is the electric field applied in the x-direction. The conductivity of the sample is given by

$$\sigma = \sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 \qquad (4)$$

where σ_1, σ_2 etc. are the individual conductivities, which may be expressed by the products of the number of electrons or holes with

their corresponding mobilities, μ_1, μ_2, μ_3 or μ_4.

$$\sigma_1 = e\,\nu_1\mu_1 \quad , \quad \sigma_2 = e\,\nu_2\mu_2 \quad , \quad \sigma_3 = e\,\nu_3\mu_3$$
$$\text{and} \quad \sigma_4 = e\,\nu_4\mu_4 \quad . \tag{5}$$

In Eqs. (5), $\nu_1 = \nu_2 = n_e/2$ while ν_3 = the number of holes/atom and ν_3 = the effective number of electrons/atom in the parallel half of the 3d sub-band and ν_4 = the number of holes/atom and ν_4 = the effective number of electrons/atom in the antiparallel half of the 3d sub-band. If the 3d band is split into sub-bands, the effective number of electrons/atom will be different from the total number of electrons in this 3d band.

It is convenient to introduce a convention for the signs of the carriers and their mobilities. This convention states that, whenever the Hall effect due to the i-th band is n-type, ν_i will be a positive number representing the number of electrons/atom in this band and μ_i will be a positive number representing their mobility. When, however, the Hall effect due to the i-th band is p-type, ν_i will be a negative number representing the number of holes/atom in the band and μ_i will be a negative number representing the mobility of these holes. This convention eliminates the confusion caused by carrying the plus-or-minus sign in the multiple band equations for the Hall constants. Obviously the product $\mu_i\,\nu_i$ must have the plus sign for either holes or electrons, since the conductivity is always positive.

Now the measured Hall emf is given by

$$E_y = E_{y1} + E_{y2} + E_{y3} + E_{y4} \tag{6}$$

and the method of measuring this emf with a potentiometer guarantees

that the net current in the y-direction is zero. Hence

$$\sigma_1 E_{y1} + \sigma_2 E_{y2} + \sigma_3 E_{y3} + \sigma_4 E_{y4} - \sigma E_y = 0 \ . \qquad (7)$$

The individual Hall emf's are given from Eq. (3) by

$$E_{y1} = R_{o1} H \sigma_1 E_x + R_{11} M \sigma_1 E_x$$

$$E_{y2} = R_{o2} H \sigma_2 E_x + R_{12} M \sigma_2 E_x \ , \text{ etc.} \qquad (8)$$

Multiplying each equation in (8) by its corresponding σ and substituting in Eq. (7) the following equation is obtained

$$\sigma E_y = H E_x \sum_j \sigma_j^2 R_{oj} + M E_x \sum_j \sigma_j^2 R_{1j} \ . \qquad (9)$$

Experimentally, at least in ferromagnetic materials, the Hall effect proportional to M can be separated[16] from that proportional to H. Hence, Eq. (9) can be combined with Eq. (3) and separated into two equations,

$$\sigma^2 R_o = \sum_j \sigma_j^2 R_{oj}$$

and

$$\sigma^2 R_1 = \sum_j \sigma_j^2 R_{1j}$$

16/ C. J. Kevane, S. Legvold and F. H. Spedding, Phys. Rev. 91, 6, 1372-1379, (Sept. 15, 1953) separate these two effects in gadolinium by means of their different temperature dependence.

By means of Eqs. (5) these can be written

$$\sigma^2 R_o = e^2 \sum_j \mu_j^2 \nu_j^2 R_{oj} \qquad (10)$$

and

$$\sigma^2 R_1 = e^2 \sum_j \mu_j^2 \nu_j^2 R_{1j} \quad \underline{17/} \quad . \qquad (11)$$

Equation (10) is identical to the Jones-Zener equation for two bands, if $R_{oj} = -1/N\ \nu_j$ ec and j takes the two values 1 and 2. Thus, if the bands are either nearly empty or nearly filled so that $R_{oj} = -1/N\ \nu_j$ ec is a good approximation,

$$R_o Nec = - \sum_j \left(\frac{\sigma_j}{\sigma}\right)^2 \frac{1}{\nu_j} \quad . \qquad (10')$$

Actually, Eq. (10') is generally a good approximation for Eq. (10) whenever any one of the bands is either nearly empty or nearly full. If the R_o for each band behaves like the R_o shown in Fig. 2, significant contributions to the summation must come only from those bands that are nearly full or nearly empty. Thus the bands in which the approximation is valid make large contributions while those in which the approximation is invalid make only small contributions.

In ferromagnetic materials in which the 3d conduction can be neglected; e.g. in the alloys 80 Ni-20 Cu and 62 Ni-38 Co, Eq. (10)

17/ J. M. Luttinger and Robert Karplus, have calculated R_1 from spin-orbit coupling and their equation provides the right order of magnitude and the observed temperature dependence, neither of which have been obtained before. It does not appear to provide the observed dependence on alloy composition. Their equation does not come out in the form of Eq. (11). To put Eq. (11) in the form given by Luttinger and Karplus, one should assume $R_{11} \cong R_{12} \cong R_{14} \cong 0$ and $R_{13} \cong A/\sigma_3^2$. However, if it is assumed instead that $R_{13} = A/\sigma_3\mu_3$, Eq. (11) will provide the observed dependence on both alloy composition and temperature. Some modification of this sort is needed to account for the experimental fact that the extraordinary coefficient R_1 changes sign by passing through zero at nearly the Co-Ni alloy composition where the ordinary coefficient R_{o3} changes sign by passing through zero.

gives $R_o Nec = -1/\nu_1 = -2/n_s$ at low temperatures where $\mu_1 >> \mu_2$ and $R_o Nec = -1/2\,\nu_1 = -1/n_s$ above the Curie temperature where $\mu_1 = \mu_2$. Intermediate values are obtained at intermediate temperatures which accounts for the temperature dependence observed in R_o for the Cu-Ni alloys lying between 50 and 90 percent Ni. The measured values of R_o for these alloys which are shown in Fig. 3 agree with the predictions of Eq. (10) using only j = 1 and 2. The Ni-Co alloys have been measured only at room temperatures, which must be considered as low temperatures since their Curie temperatures are high.

It is desirable to determine whether or not Eq. (10) can account for the low values of R_o found in the Ni-rich alloys with reasonable values of μ_3 and μ_4. If the mobilities needed to explain the ordinary Hall data are reasonable they should be able to account for the observed resistivities at the various temperatures. Since pure Ni has the smallest Hall constant of the Ni-rich group it will be treated in most detail.

Nickel

Fortunately values of ρ in Ni are relatively simple to calculate from the Hall coefficients since above the Curie temperature, $\nu_3 = \nu_4 = -n_s/2$. Furthermore, below the Curie temperature, these numbers are determined rather simply from $m = M_s/M_o$, the ratio of the saturation magnetization at the given temperature to that at

absolute zero. That is,

$$\nu_3 = -(1 - m)n_s/2 \ ,$$
$$\nu_4 = -(1 + m)n_s/2 \qquad (12)$$

and $$\nu_1 = \nu_2 = n_s/2$$

at all temperatures.

To calculate R_o it is necessary to know the relative mobilities in the four bands. According to Mott[10], 4s electrons with a given spin can be scattered only by holes in that half of the 3d band that has the same spin. Hence the ratio $\beta = \mu_2/\mu_1$ should depend upon ν_4/ν_3. Assume Mott's[10] relation $\beta = (\nu_4/\nu_3)^{1/3}$. The ratio μ_4/μ_3 is less certain, but $\mu_4/\mu_3 \cong \beta$ may be a reasonable assumption. Fortunately, the results obtained are not at all critically dependent upon this last assumption. Finally the ratio $\delta = -\mu_3/\mu_1$ must be considered as an unknown which can be determined from the Hall data. The experimental values of δ can then be used to calculate resistivity as a function of temperature, from

$$\sigma = \sum_j \sigma_j = e \sum_j \nu_j \mu_j \ .$$

Thus, with the foregoing assumptions

$$\sigma = \sigma_1 \left\{ 1 + \beta + (1 - m)\delta + (1 + m)\beta\delta \right\} \qquad (13)$$

and from Eqs. (10') and (12)

$$\sigma^2 R_o = \sigma_1^2 R_{o1} \left\{ 1 + \beta^2 - (1 - m)\delta^2 - (1 + m)\beta^2 \delta^2 \right\} \qquad (14)$$

which can be written as

$$\sigma = \sigma_1 \{ 1 + \beta + \alpha\delta \} \qquad (13')$$

and

$$\{ 1 + \beta + \alpha\delta \}^2 = r\{ 1 + \beta^2 - \gamma\delta^2 \} \qquad (14')$$

where

$$\alpha = (1 - m) + (1 + m)\beta$$

$$\gamma = (1 - m) + (1 + m)\beta^2 \quad \text{and} \quad r = R_{o1}/R_o \ .$$

Solving (14') for

$$\delta = \frac{\left\{ r(\alpha^2 + r\gamma)(1 + \beta^2) - r\gamma(1 + \beta)^2 \right\}^{\frac{1}{2}} - \alpha(1 + \beta)}{\alpha^2 + r\gamma} \ . \qquad (15)$$

The values for r at different temperatures are obtained from the Hall data. Figure 3 shows that, for the purest Ni measured $R_o \cong -5.9 \times 10^{-13}$ ohm-cm/oersted at low temperatures and changes very little with temperature up to room temperature.[18] Data on pure Ni is not available above room temperature, but the old data of A. W. Smith[19] suggests that the ordinary Hall coefficient for

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18/ This statement is based upon measurements in this laboratory by Philip Cohen on two different samples of Ni; one being 99.9% pure and the other 99.99% pure. Both were carefully annealed in an He atmosphere. J. P. Jan and H. M. Gijsman; Physica, 18, 5, 277-360 Amsterdam (May 1952) report R_o's for their Ni sample from 5.5×10^{-13} at room temperature to 3.0×10^{-13} at liquid hydrogen temperatures. J. Smit and J. Volger; Phys. Rev. 92, 6, 1577(Dec. 15, 1953) R_o's (A_H in their symbols) for four different samples of Ni at 20 °K, 77 °K and 290 °K that vary from 3.6×10^{-13} to 13.3×10^{-13}. One of their samples varies only slightly with temperature.

19/ E. M. Pugh, N. Rostoker and A. I. Schindler, Phys. Rev. 80, 4, 688-692 (Nov. 15, 1950).

Ni remains essentially constant through the Curie temperature. The values of $\delta = \mu_3/\mu_1$ needed to produce the observed Hall effect in Ni can be obtained from Eq. (15) by setting r = 4.3.

At the Curie temperature this mobility ratio δ is 0.365. Since in Ni the number of 3d holes equals the number of 4s electrons, this indicates that at and above the Curie temperature, 27 percent of its conductivity is due to the holes. Below the Curie temperature δ increases with decreasing temperature, slowly at first and more rapidly as the absolute zero is approached.

This increase in δ toward absolute zero suggests that as the parallel 3d band is filled, the few remaining holes acquire a high mobility. However, the antiparallel 3d band does not fill up and the holes in it should not acquire this high mobility. It probably has little effect on the Hall constant at low temperatures. This indicates that one of our assumptions cannot be valid at very low temperatures. The ratio, μ_4/μ_1, is probably equal to $\beta\delta$ at the Curie temperature as has been assumed but is probably more nearly equal to a constant times β at low temperatures. Since at the Curie temperature $\delta = 0.365$, the fourth term in the brackets of Eq. (13) should be written as $0.365(1 + m)\beta$ and the fourth term in the brackets of Eq. (14) should be written $-(0.365)^2(1 + m)\beta^2 = -0.133(1 + m)\beta^2$. In any case, these terms are too small to affect the result very much.

The modified Eqs. (13) and (14)

$$\sigma = \sigma_1\left\{1 + \beta + (1 - m)\delta + 0.365(1 + m)\beta\right\} \qquad (13')$$

$$\sigma^2 R_o = \sigma_1^2 R_{o1}\left\{1 + \beta^2 - (1 - m)\delta^2 - 0.133(1 + m)\beta^2\right\} \qquad (14')$$

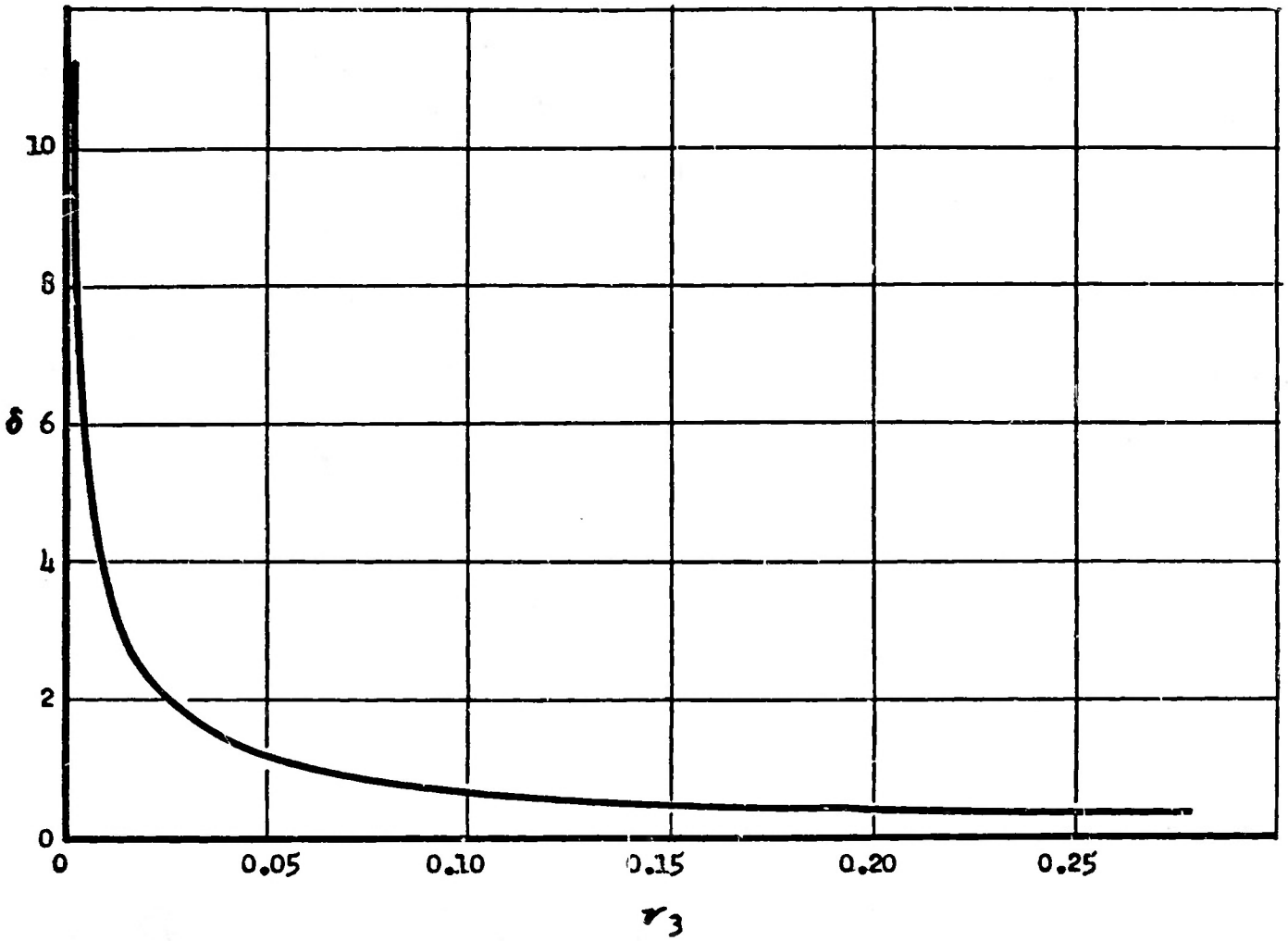

Fig. 6 Plot of δ, the relative mobility of the holes in the parallel 3d band compared to the mobility of the electrons in the parallel half of the 4s band, against ν_3, the holes/atom in this 3d band.

can now be combined and solved for δ . In Fig. 6 the new values of δ are plotted versus $|\nu_3|$, the number of holes in the parallel 3d band. Values of δ are quite high for small values of $|\nu_3|$, but as $|\nu_3|$ increases δ approaches the constant value of 0.365. Probably the large hole mobilities in the parallel 3d band ($\mu_3 = \delta\mu_1 > \mu_1$) are to be found only in relatively pure Ni which is well annealed. Probably, too, the values of δ at low temperatures are quite sensitive to the nature of the impurities and to the state of anneal. This may account for the different R_o's reported for Ni by other observers.[18]

If the assumptions employed in accounting for the Hall effect data are reasonable, they must be capable of accounting for the resistivities. In particular one wonders whether or not the large values of μ_3 required to account for the low temperature Hall data on Ni are consistent with the observed variation in resistivity with temperature.

Resistivity of Nickel

The resistivity of Ni could be calculated directly from Eq. (13') if σ_1 were known as a function of temperature. However, even if σ_1 were known exactly one should not expect perfect agreement with experiment. While the assumptions used in Eq. (13') are consistent with modern band models, they are nevertheless somewhat arbitrary. For example, the assumption, due to Mott, that $\mu_2/\mu_1 = (\nu_4/\nu_3)^{1/3}$, is based upon spherical symmetry and cannot be considered exact. Nevertheless, with these assumptions the Hall data on Ni yields numerical constants which are consistent with the observed resistivities of Ni.

Considering 4s band conduction only, one can see that the resistivity of Ni, Co, and Fe around -180°C qualitatively bear the expected relation to the resistivity of Cu at this temperature. If Ni and Co have 0.28 highly mobile 4s electrons/atom while Cu has 1.0, the resistivities of Ni and Co should be near 1.0/0.28 or 3.6 times that of Cu, which is close to that observed. In Fe there are holes in both the parallel and antiparallel 3d bands so that none of its 4s electrons should have high mobility. As should be expected its resistivity is greater than the others, being about 5.5 times that of Cu.

Now σ_1 is that part of the conductivity that can be ascribed to the 4s electrons with parallel spins. The corresponding resistivity, $\rho_1 = 1/\sigma_1$ can be divided into three parts due to (1) scattering by lattice vibrations, (2) scattering by holes in the 3d band, and (3) scattering by impurities. Assuming no impurities the last can be ignored. The first can be calculated from the resistivity of Cu and the second can be calculated from the resistivity of Ni above the Curie temperature. Mott[10] has pointed out that the temperature dependence of ρ is the same for Ni above its Curie point as it is for Pd in the same temperature region. He concludes that the two should have the same temperature dependence at all temperatures if Ni remained paramagnetic at low temperatures. This similarity stems from the two having such similar band structures, with approximately 0.6 electron/atom in the s shell and approximately 0.6 holes/atom in the d shell.

That part of ρ_1 that is due to lattice vibrations should be given by $\rho_{le} = (\theta_{Cu}/\theta_{Ni})^2(1.0/0.28)\rho_{Cu}$ where θ_{Cu} and θ_{Ni} are the

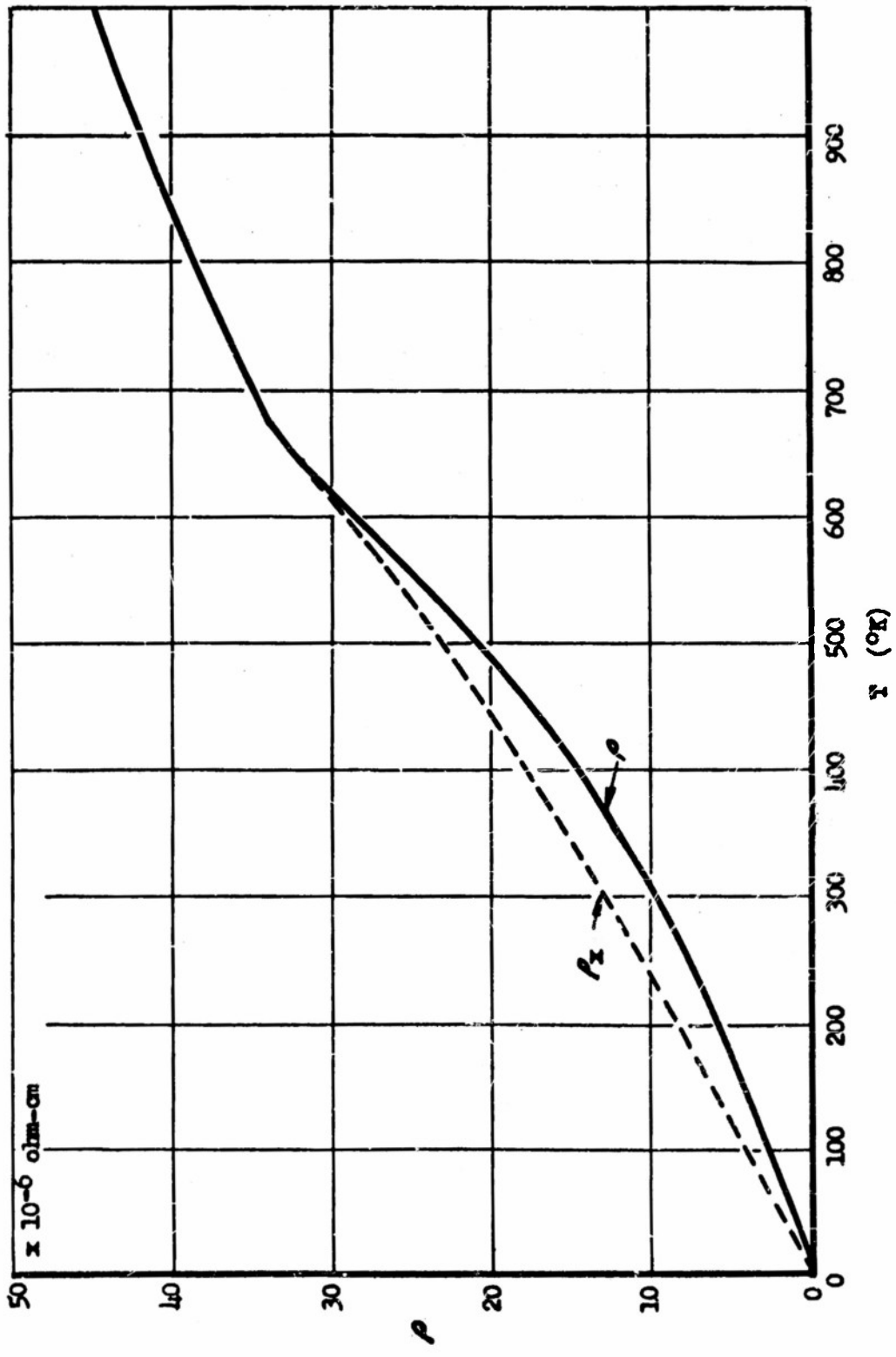

Fig. 7 Plot showing the observed resistivity of Ni, ρ, compared to the resistivity Ni should have if it remained paramagnetic to low temperature. The ρ_x is calculated from Hall effect data.

Debye temperatures for these elements. This is

$$\rho_{le} = 2.57\ \rho_{Cu}$$

Calculating the part of ρ_l due to scattering by holes is more difficult. Above the Curie temperature there is a constant ratio between ρ_l and ρ, given by either Eq. (13) or (13'); namely

$$\rho_l = 2.73\ \rho \ , \text{ since } m = 0 \text{ and } \beta = 1 \ .$$

Above the Curie point then, the part of ρ_l due to scattering by holes is $\rho_{lh} = 2.73\ \rho - 2.57\ \rho_{Cu}$. If we call ρ_x the resistivity Ni would have if it remained paramagnetic to low temperatures, then the value of ρ_{lh} under these same conditions would be $2.73\ \rho_x - 2.57\ \rho_{Cu}$. However, the number of holes/atom into which the parallel s electrons can scatter is given by (1-m)0.28 and

$$\rho_{lh} = (1 - m)^{1/3}(2.73\ \rho_x - 2.57\ \rho_{Cu})$$

and

$$\rho_l = 2.57\ \rho_{Cu} + (1 - m)^{1/3}(2.73\ \rho_x - 2.57\ \rho_{Cu})$$

but from Eq. (13')

$$\rho_l = \rho\left\{ 1 + \beta + (1 - m)\delta \ + 0.365(1 + m)\beta \right\} .$$

Combining these last two equations ρ, the resistivity of Ni, can be calculated provided ρ_x is known. This can be obtained by using the resistivity versus temperature curve of Pd to extrapolate the high temperature Ni data to low temperatures.

It is simpler, however, to use the observed ρ versus T data on Ni to calculate ρ_x to compare with the Pd curve. In Fig. 7 the observed Ni data (ρ versus T) and the calculated "paramagnetic"

nickel curve (ρ_x versus T) are plotted. This latter curve is much like the Pd curve though it still changes direction a little too rapidly around the Curie temperature. Actually the shape of this curve is quite sensitive to the value of the exponent b in the relation $\beta = \mu_2/\mu_1 = (\nu_4/\nu_3)^b$ which is 1/3 for spherical symmetry. Only a small increase in b above 1/3 is required to eliminate the rapid change in direction of the ρ_x curve at the Curie point. Thus the resistivity data on Ni is consistent with this simple band model.

Conclusions

The ordinary Hall constants for Co, Ni, Cu and their binary alloys, measured at different temperatures, can be understood on the basis of a simple four band model. The four bands consist of the two halves of the 4s band with spin parallel and antiparallel to the magnetic field and two sub-bands of the 3d shell also having spins parallel and antiparallel.

It appears that the resistivities of these materials also can be understood on the basis of the same four band model. Actually only the resistivity of Ni as a function of temperature has been worked out in detail but this had appeared, at the outset, to be the most doubtful case.

Since all of the calculations have used the saturation magnetization data to determine the number of carriers in each band, the saturation magnetization data is also consistent with this model.

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